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Thermoelectric properties and micro-structure characteristics of annealed N-type bismuth telluride thin film

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ABSTRACT

N-type bismuth telluride (Bi_2Te_3) thermoelectric thin films were deposited by co-sputtering simple substance Te and Bi targets. The deposited films were annealed under various temperatures. The composition ratio, micro-structure and thermoelectric properties of the prepared films were systematically investigated by energy dispersive spectrometer, X-ray diffraction, four-probe method and Seebeck coefficient measurement system. When the annealing temperature is 400 °C, the stoichiometric N-type Bi_2Te_3 film is achieved, which has a maximum thermoelectric power factor of 0.821×10^{-3} W m^{-1} K^{-2}. Furthermore, the dependence of Seebeck coefficient, electrical conductivity and power factor of the stoichiometric N-type Bi_2Te_3 film annealed at film 400 °C on the applied temperature ranging from 25 °C to 315 °C was investigated. The results show that a highest power factor of 3.288×10^{-3} W m^{-1} K^{-2} is obtained at the applied temperature of 275 °C. The structural and thermoelectric properties of the deposited bismuth telluride thin films are greatly improved by annealing and the Seebeck coefficient, electrical conductivity and power factor increase with the applied temperature rising, which are helpful and could be guidance for preparing the high-performance thin film thermoelectric materials for thermoelectric application.

1. Introduction

Thermoelectric techniques are used in a wide temperature range as power generators, solid-state coolers and sensors due to many attractive features, such as clean and noiseless energy without discharging any hazardous substance, high reliability and long life time [1]. Significant progress has been made in recent years and it indicates that low-dimensional materials have high thermoelectric conversion efficiency [2,3]. Thermoelectric thin film is one of the important low-dimensional thermoelectric materials due to its stronger quantum confinement compared with that of their bulk materials quantum confinement, a potentially more favorable carrier scattering mechanism, and a much lower lattice thermal conductivity [4–8]. Bi_2Te_3 is a widely employed thermoelectric material that has high ZT (defined as $ZT = \alpha^2 \sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the temperature) at room temperature [9–11]. Many studies have been done to fabricate Bi_2Te_3 thin films by physical vapor deposition (PVD) or chemical vapor deposition (CVD) techniques and the research had found that the films have great TE properties [12–14]. In comparison to other methods, DC and RF magnetron sputtering are the most attractive techniques for industrial development and possibility of using commercially available large area sputtering systems [15–17]. However, because of the high vapor pressure of Te, it is difficult to obtain stoichiometric Bi_2Te_3 thin films by magnetron sputtering technology. Therefore, the properties of Bi_2Te_3 thin films prepared by DC or RF magnetron sputtering are often unsatisfactory.

For preparing high performance of Bi_2Te_3 thin film by magnetron sputtering for low-cost thermoelectric application, in this paper, the Bi_2Te_3 films were fabricated by RF and DC co-sputtering with the simple substance Te and Bi targets instead of the traditional Bi_2Te_3 target. The annealing temperature was varied from 250 °C to 450 °C in order to investigate the influence of annealing temperatures on thermoelectric properties and structure of the Bi_2Te_3 films. The composition ratios, crystal structure and thermoelectric properties of the Bi_2Te_3 films were investigated systematically.

2. Experimental details

Bismuth telluride thin films were deposited on BK7 glass substrates at room temperatures with a multi-target sputtering system. High purity Bi (99.99%) and Te (99.99%) targets with a

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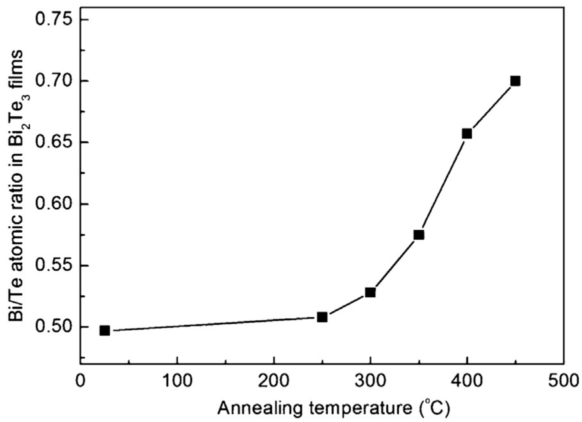

Fig. 1. The atomic ratio of Bi to Te in bismuth telluride thin films annealed at different temperatures.

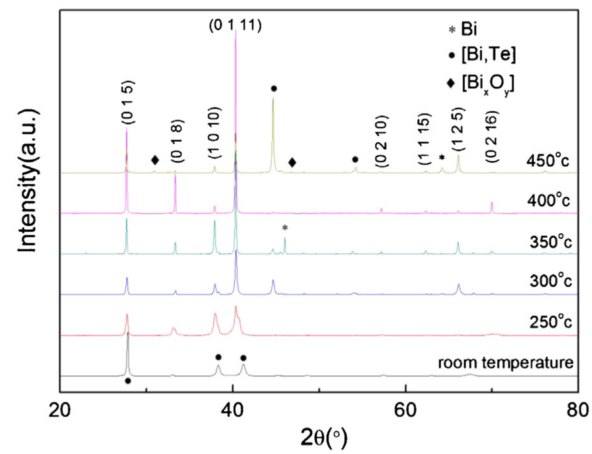

Fig. 2. XRD patterns of the bismuth telluride thin films annealed at different temperatures.

diameter of 60 mm were used. The substrates were ultrasonically cleaned in acetone and alcohol for 10 min respectively. In our early research, we found that the target with the same height and angle toward the substrate always achieved worse Bi_2Te_3 thin film. So, in this work, the incident angle of Bi is set about 50° and the Te is set about 40°. The distance between the central point of the target and the substrate was about 100 mm of Bi and 130 mm of Te. The chamber was pumped down to a pressure less than 6.0×10^{-4} Pa prior to deposition. The working pressure was controlled at 0.30 Pa with 40 sccm of Ar as the sputtering gas. The RF power of Te target was 80 W and the DC power for sputtering Bi target was 7.2 W. Bismuth telluride thin films were deposited at room-temperature and the deposition time was 30 min, with a film thickness of 1.03 μm. The films were annealed at the temperatures of 250 °C, 300 °C, 350 °C, 400 °C, 450 °C. The annealing pressure was 470 Pa with Ar as the annealing gas and the annealing time is 1 h.

The thicknesses of the films were measured by using a DEKTAK3 ST surface-profile measurement system. The composition ratios of the thin films were determined using an energy dispersive X-ray spectroscopy (EDS) microanalysis system. The crystal structure of the films was studied by X-ray diffraction (XRD) technique (BRUKER-D8-ADVANCE). The samples were scanned from 20° to 80° in the θ–2θ mode. The thermoelectric properties of thin films were measured by using the four-probe method and Seebeck coefficient measurement system (SDFP-I). The electric conductivity (σ) was calculated using Eq. (1) and power factor (PF) was obtained from Eq. (2) (ρ is electric resistivity, V/I is measured by the four-probe method, d is the thickness of the films, α is the Seebeck coefficient).

$$\sigma = \frac{1}{\rho} = \frac{1}{(\pi/\ln 2) \times (V/I) \times d} \qquad (1)$$

$$PF = \alpha^2 \sigma \qquad (2)$$

3. Results and discussion

Since the thermoelectric property of Bi_2Te_3 film strongly depends on its stoichiometry, it is crucial to investigate the atomic ratios of Bi to Te in Bi_2Te_3 thin films. Fig. 1 shows the atomic ratios of Bi to Te in bismuth telluride thin films at various annealing temperature. It is found that atomic ratio of Bi to Te in bismuth telluride thin films increases from 0.497 to 0.701 with the annealing temperature increasing to 450 °C. This phenomenon is mainly due to the evaporation of Te during annealing. Nearly stoichiometric Bi_2Te_3 film is achieved when the annealing temperature is 400 °C.

Fig. 2 shows the XRD patterns of bismuth telluride thin films annealed at various temperatures. As can be seen from Fig. 2, the thin film deposited at room temperature has the highest impurity peaks corresponding to the (1 0 4) planes of [Bi,Te]Te. After annealing, it can be found that three major diffraction peaks of Bi_2Te_3 films are located at 27.961°, 33.292° and 38.021°, which are indexed as the reflection from the (0 1 5), (0 1 8) and (0 1 11) of Bi_2Te_3 [18–20]. As the annealing temperature increases from 250 to 400 °C, the intensity of the three major diffraction peaks enhances. Other small peaks such as (1 0 10), (0 2 10), (1 1 15), (1 2 5) and (0 2 16) also belong to their characteristics diffraction peaks, which indicates that a hexagonal structure belonging to the R-3m space group of Bi_2Te_3 film is dominant and the grain gets larger and the crystalline quality improved after annealing. When the annealing temperature reaches 400 °C, the intensity of the major diffraction peaks gets the highest and the film has the (0 1 11) preferred phase. This will indicate that the film annealed at 400 °C can has better crystalline quality. Because of evaporation of Te elements and oxygen traces at higher temperature, the intensity of the three major diffraction peaks decrease and the impurity peaks related to some [Bi,Te]Te and [Bi_xO_y] can be observed at 450 °C. From the XRD results, it can be concluded that Bi_2Te_3 thin films of high crystalline quality are obtained after annealing. By improving the crystalline quality, the defects reduced, interface and impurity scattering may also reduce. These changes are considered to make contribution to the improvement of thermoelectric performance of Bi_2Te_3 thin film.

Fig. 3 shows the Seebeck coefficient and conductivity of the bismuth telluride thin films annealed at different temperatures with the test temperature of 25 °C. As shown in Fig. 3, the negative Seebeck coefficient implies that the bismuth telluride film is n-type. The Seebeck coefficient absolute values increases from 49 to 177 $\mu V K^{-1}$ with the annealing temperature rising, and electrical conductivity increases from 3.14×10^4 to 5.51×10^4 S cm^{-1} as the temperature increases from room temperature to 400 °C. However, when the annealing temperature reaches 450 °C, the conductivity significantly decreases to 0.51×10^4 S cm^{-1}. The electrical properties of the film grown at room-temperature are worse, this might be due to its crystal defects caused by poor crystalline quality at room-temperature. Therefore, annealing was used to improve the thermoelectric properties of the films. The change of Seebeck coefficient is mainly ascribe to the improvement of crystal lattice scatter. The enhancement of conductivity is mainly due to evaporation of Te at high annealing temperature, resulting in less impurity scattering. Those superfluous Te atoms which did not make a compound with Bi atoms were evaporated around the annealing

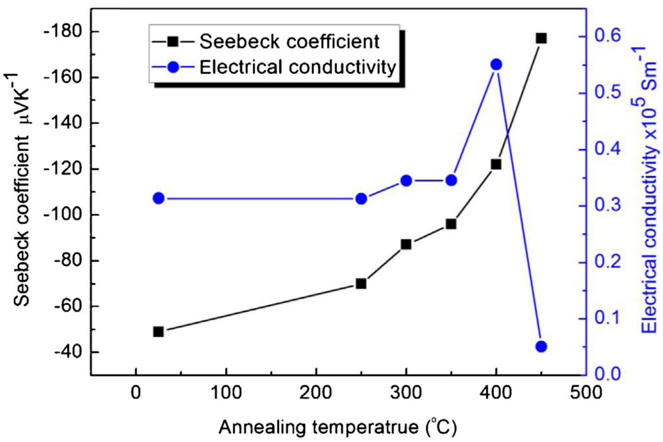

Fig. 3. Seebeck coefficient and conductivity of the bismuth telluride thin films annealed at different temperatures.

temperature. Compared with the change of the conductivity annealed from room-temperature to 400 °C, the conductivity decreases greatly when the annealing temperature ranges from 400 °C to 450 °C. This might result from increase of impurity at a extortionate temperature, which leads to great enhancement of impurity scattering and the conductivity decreases significantly.

Fig. 4 illustrates the power factor of the bismuth telluride thin films annealed at different temperatures with the test temperature of 25 °C. As shown in Fig. 4, the power factors are in the range of 0.069×10^{-3} to $0.821 \times 10^{-3}\,\mathrm{W\,m^{-1}\,K^{-2}}$ as the temperature increases from room temperature to 450 °C. The film annealed at 400 °C has a maximum PF value of $0.821 \times 10^{-3}\,\mathrm{W\,m^{-1}\,K^{-2}}$ because of the high Seebeck coefficient and enhanced electric conductivity. The results demonstrate that annealing can indeed improve the thermoelectric properties of the film and the enhanced thermoelectric properties can be obtained with the optimal annealing temperature of 400 °C.

Fig. 5 shows the effect of the applied temperature on Seebeck coefficient, electrical conductivity and power factor of the film annealed at 400 °C in the range from 25 °C to 315 °C. As shown in Fig. 5(a), the Seebeck coefficient absolute value increases as the applied temperature increases in the range of 25 °C to 315 °C and the maximum absolute value of Seebeck coefficient, $320\,\mu\mathrm{V\,K^{-1}}$, is achieved with the applied temperature of 315 °C. When the temperature is below 275 °C, the electrical conductivity of the film shows a semiconducting-like behavior, it increases with the

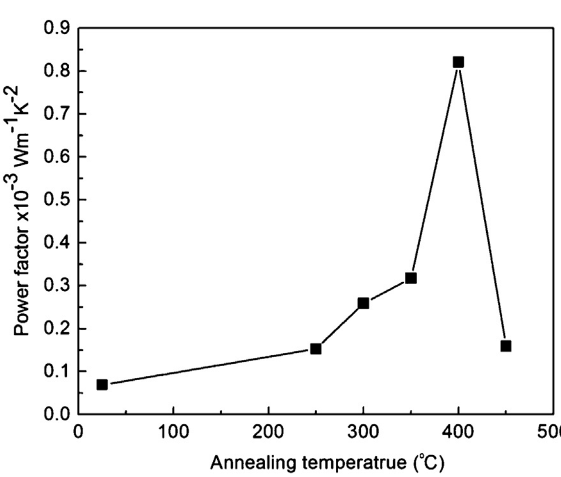

Fig. 4. Power factor of the bismuth telluride thin films annealed at different temperatures.

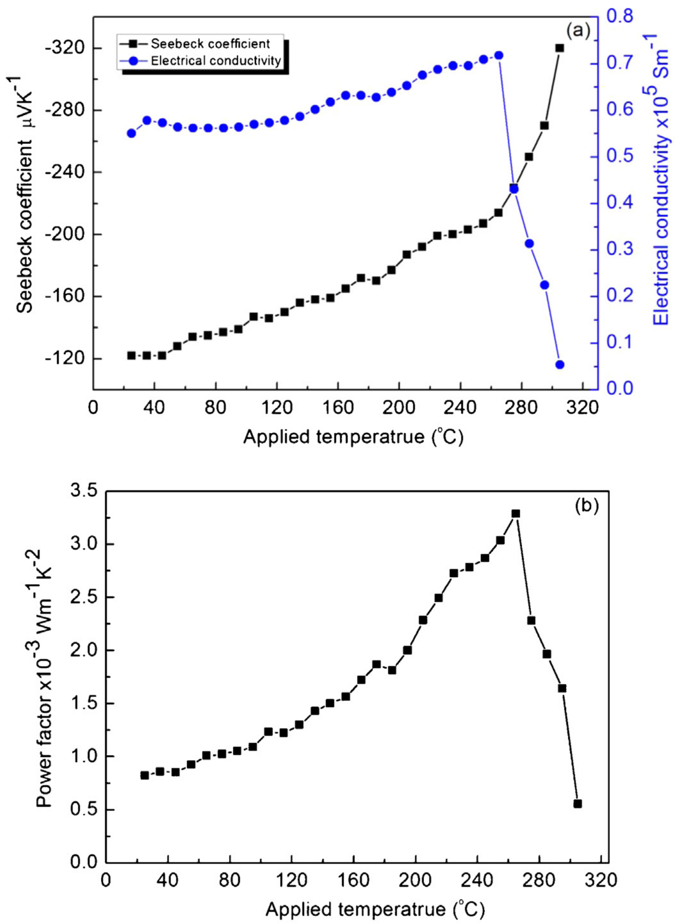

Fig. 5. The effect of applied temperature on Seebeck coefficient, electrical conductivity and power factor of the film annealed at 400 °C. (a) Seebeck coefficient and electrical conductivity (b) power factor.

temperature increasing. When the applied temperature is above 275 °C, the electrical conductivity of the film decreases with the temperature increasing further. It might be owing to the fact that the testing background is full of oxygen gas and the films will absorb the oxygen at high temperature atmosphere. The relation between power factor and temperature is plotted in Fig. 5(b), a highest power factor of $3.288 \times 10^{-3}\,\mathrm{W\,m^{-1}\,K^{-2}}$ is obtained at the temperature of 275 °C.

4. Conclusions

N-type Bi_2Te_3 thermoelectric thin films were grown on glass substrates by using DC and RF magnetron co-sputtering method. The annealing temperature was varied from 250 °C to 450 °C in order to investigate the influence of annealing temperature on the Bi_2Te_3 films. EDS and XRD results demonstrate that the stoichiometric N-type Bi_2Te_3 film with improved crystalline quality is achieved when the annealing temperature is 400 °C. It is found that the Seebeck coefficient absolute value increases from 49 to $177\,\mu\mathrm{V\,K^{-1}}$, electrical conductivity increases from 3.14×10^4 to $5.51 \times 10^4\,\mathrm{S\,cm^{-1}}$ and the power factor is in the range of 0.069×10^{-3} to $0.821 \times 10^{-3}\,\mathrm{W\,m^{-1}\,K^{-2}}$ while the annealing temperature varies from room temperature to 450 °C. The effect of the applied temperature on the thermoelectric properties of the film annealed at 400 °C shows that the Seebeck coefficient absolute value, electrical conductivity and power factor increase as the applied temperature increase. When the temperature reached 275 °C, a highest power factor of $3.288 \times 10^{-3}\,\mathrm{W\,m^{-1}\,K^{-2}}$ is

obtained. These results demonstrate that high performance Bi_2Te_3 thin films can be prepared by DC and RF magnetron co-sputtering with post-annealing. The technology employed in this work provides a promising procedure for fabricating thin film thermoelectric generator.

Acknowledgments

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